DRAFT - The words may change But the content won't
To be published
Fall 1991 @
GRC

ARSENIC SPECIATION IN ATMOSPHERIC AEROSOLS AT THE GEYSERS

Paul A. Solomon
Samuel L. Altshuler
Clint D. Gans
Marilyn L. Keller

Pacific Gas and Electric Company
Department of Research and Development
and Technical and Ecological Services
3400 Crow Canyon Road
San Ramon, CA 94583

ABSTRACT

Geothermal energy production in California has been identified as a major source of arsenic by the California Air Resources Board. New regulations have been implemented by the State of California, which require information on ambient levels and emissions of inorganic arsenic. However, these laws consider only total arsenic and do not take into account the potential differences in toxicity and perhaps even carcinogenicity of the different arsenic species present in the ambient atmosphere. In response to that need, atmospheric particulate matter samples were collected at The Geysers geothermal development area in Lake County California over a two month period in 1989. This paper describes those results and provides, for the first time, insight into the atmospheric loadings of the inorganic species of arsenic, As(III) and As(V), at geothermal power facilities.

INTRODUCTION

REGULATIONS AND RISK ASSESSMENT

California's air toxic law (AB 1807), which became effective in January 1984, defines California's air toxic program (California Department of Health Services [DHS] 1984). Under this legislation, a statutory mandate was created for the identification and control of toxic air contaminants found in California.

Ambient concentration is one of the mandated criteria used in the identification process to prioritize compounds that are believed hazardous to human health. The California Air Resources Board (ARB) has developed a list of potentially toxic substances based on this mandated ambient criteria. Inorganic arsenic is required to be on this list, because it has been identified as a hazardous air pollutant under Section 112 of the U.S. Clean Air Act.

Inorganic arsenic is listed by the ARB under Category I: substances under review for the identification as a toxic air contaminant (ARB 1990a). This category describes substances which have been identified as Toxic Air Contaminants by the ARB, pursuant to the provisions of AB1807.

The DHS (ARB 1990c) estimates the number of excess cancer deaths or risk due to airborne inorganic arsenic exposure in California's South Coast and San Francisco Bay Area air basins to be 1-25 cases per ng m^{-3} per million persons. This is based on a 1986 average ambient population-weighted concentration of arsenic equal to 1.9 ng m^{-3} for those two air basins. The lower end of the range (1-2) corresponds to nonsmokers, whereas the upper end (10-25) corresponds to males who smoke heavily. Higher risks may occur near sources. However, the DHS also concludes that it is unlikely that carcinogenic adverse health effects would be caused by current ambient levels of arsenic in California. Statewide concentrations, based on 1986 data, are about 32% lower; therefore, the risk based on the 1986 statewide data would be lower by an equivalent percentage, since a linear model is assumed in calculating the risk assessment.

The risk due to ambient exposures of inorganic arsenic in California, as reported by the DHS, is in the same range as that reported by the Environmental Protection Agency, based on its health assessment of inorganic arsenic (EPA 1984). However, both risk estimates are based on a number of assumptions that are summarized in their respective documents.

Inorganic arsenic also is included in the list of substances under California's Air Toxic "Hot Spots" Information and Assessment Act of 1987 (AB 2588) (DHS 1987). This law became effective in September 1987 and requires the ARB to compile and maintain a list of substances, which are referenced in AB 2588. Arsenic is identified under Category 1: substances required to be on the AB 2588 list by Health and Safety Codes 44321 (c), (d), (e), and (f).

The health effects information and risk assessments for arsenic, however, only consider total arsenic and not the individual species of inorganic arsenic present in the atmosphere (EPA 1984; ARB 1990b, 1990c). The measurement of individual species of inorganic arsenic is particularly important because of the variations in the toxicity and carcinogenicity of the different arsenic compounds found in the environment (Lisk 1971; National Academy of Science 1971; Hernberg 1972; EPA 1978, 1984). Inorganic As(III) is not only more toxic, but also may represent a greater carcinogenic hazard than As(V).

The health effects studies used by the ARB (1990c) to determine risk levels were for occupational exposures where As(III) is believed to be the only arsenic species present; therefore, the current ARB risk assessment (ARB 1990c) may overestimate the actual risk due to inorganic arsenic in the air in California. If a substantial fraction of the arsenic in ambient air is As(V), then the true risk may be lower than the one calculated by assuming all arsenic is As(III).

ATMOSPHERIC ARSENIC

Arsenic is emitted into the atmosphere from anthropogenic and natural sources. Atmospheric concentrations of total arsenic range from about 0.01 to 0.1 ng m^{-3} in clean areas such as Antarctica (Maenhaut et al. 1979) and up to 500 ng m^{-3} near certain industrial sources such as copper smelters (Walsh et al. 1977).

In U.S. urban areas, average ambient arsenic concentrations were reported to be approximately 20 ng m^{-3} (Sawicki 1967). Annual average arsenic values measured by the National Air Sampling Network and conducted by the EPA, ranged from 2.6 to 10.9 ng m^{-3} during 1977-1981. The average over the 5-year period was 7.7 ng m^{-3} (EPA 1984). In 1986, annual average arsenic concentrations in California ranged from 0.7 to 5.0 ng m^{-3}, with an overall mean statewide concentration of 1.5 ng m^{-3}. The average for the eight southern California sites was 2.0 ng/m^3; the average for the 11 northern California sites was 1.2 ng m^{-3} (ARB 1990b). The ARB and EPA data include rural and urban areas.

In the air, arsenic is primarily associated with particles, although it also has been observed at much lower levels in the gas phase (Johnson and Braman 1975; Walsh et al. 1977, 1979; Appel et al. 1984). The predominant forms of arsenic in the atmosphere are the

inorganic oxides or oxyacids of arsenic in the +3 and +5 oxidation states. Organic arsenic compounds also have been detected in the air; however, they constitute only a small fraction of the total (Johnson and Braman 1975, Andreae 1980, Nakamura et al. 1989).

Inorganic species of arsenic (As(III) or arsenite and As(V) or arsenate) have been measured in atmospheric particulate matter at two locations: Tucson, Arizona (Solomon 1984), and the City of Industry, Los Angeles County, California (Rabano et al. 1989). The City of Industry site was located within 1 kilometer of a known high temperature source of arsenic (a secondary lead smelter [ARB 1990b]). These measurements were obtained using an analytical method that allows for the species-specific determination of As(III) and As(V) in atmospheric particulate matter with high sensitivity (Solomon 1984). Detection limits of less than 1 ng m^{-3} were achieved for both species.

The As(III)/As(V) ratio varied considerably at both locations. In Tucson, the ratio ranged from 0.04 to 0.97, with an average value of 0.31 ± 0.29. In Los Angeles, the ratio ranged from 0.26 to 2.8, with an average ratio of 1.2 ± 0.7. (A ratio of 1 indicates an equal mixture of both species.) The variations of the ratio at each site and between the two locations are most likely due to the impact of the various sources in the surrounding areas, the age of the aerosol measured at the sampling sites, and/or variations in the effective oxidation-reduction potential of the atmospheric environment (Andreae 1980; Solomon 1984).

ARSENIC AT THE GEYSERS

Arsenic is of interest at The Geysers (Figure 1), because it occurs naturally in the geothermal steam. Therefore, arsenic can be released to the atmosphere through natural venting and as the steam is used to generate power. The final ARB report on inorganic arsenic in California indicates that emissions into the atmosphere from geothermal energy production is one of the largest sources of arsenic in the state (see Table II-2 in ARB 1990b). To arrive at this conclusion, the ARB made a number of assumptions about emission rates from sources at The Geysers, some of which require verification. Therefore, it is necessary to provide regulators with accurate data on arsenic at The Geysers to ensure that imposed regulations and restrictions are justified and needed to protect public health.

The objective of this study is to obtain more accurate ambient concentration data for total arsenic and for the inorganic species of arsenic at The Geysers, which can be used to 1) determine if a long-term study is warranted and 2) advise and influence regulators in their health risk assessment for arsenic. As part of this process, an analytical method (Solomon 1984) to determine the inorganic species of arsenic (arsenite and arsenate) was established and evaluated within PG&E's Technical and Ecological Services (TES). This method was used to determine the species-specific concentrations of arsenite (As(III)) and arsenate (As(V)) in total suspended particulate matter (TSP) samples collected at The Geysers.

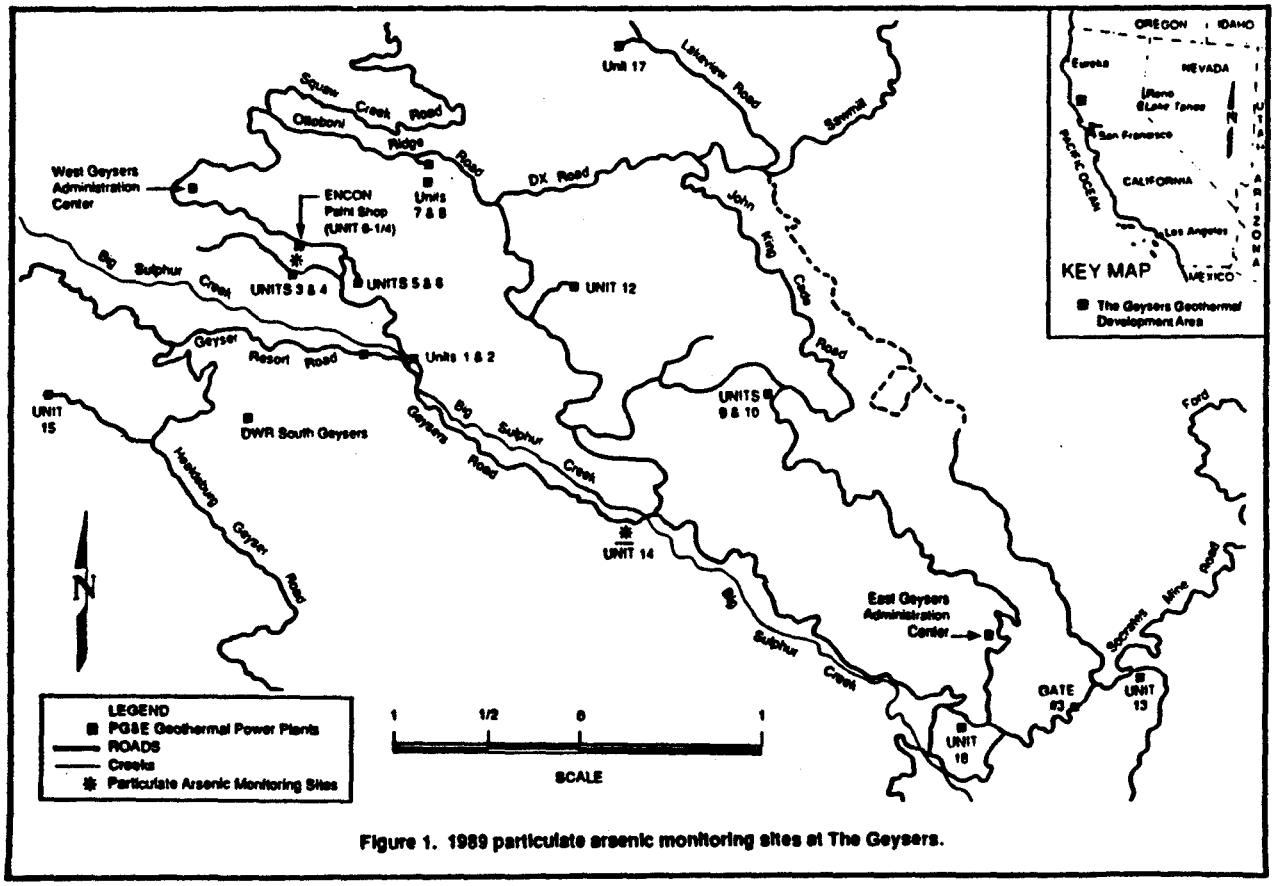

Figure 1. 1989 particulate arsenic monitoring sites at The Geysers.

EXPERIMENTAL

ATMOSPHERIC PARTICULATE MATTER COLLECTION

Atmospheric particulate matter samples were collected at two sites within The Geysers geothermal development area during April and May 1989. One site was located in the East Geysers at Unit 14, and the other was located in the West Geysers near a PG&E paint shop and just north of Units 3 & 4 (Figure 1). The locations of the sites were chosen to maximize filter loadings (i.e., near the valley floor in case an inversion occurred), while avoiding direct impact from steam vents or cooling tower drift. This approach was taken to help ensure that a sufficient amount of sample above the detection limit of the analysis method would be collected, while minimizing the influence from nearby sources.

Unit 14 is at an elevation of about 1,700 ft, which is about 800 ft below the East Geysers administration building and about 50 ft above Big Sulfur Creek, the valley floor. At this site, two samplers were placed just inside the fence perimeter near the front gate and adjacent to the industrial hygiene changing room. During the 2-month study period, Unit 14 was down for maintenance.

The site at the PG&E paint shop is at an elevation of about 2,000 ft, which is about 600 ft above the valley floor and about 300 ft below the West Geysers administration building. At this site, two samplers were placed in a field about 150 ft south of the paint shop and about 1,000 ft north of Units 3 & 4. The samplers were about 100 feet below the elevation of the paint shop and about equal in elevation with the top of the cooling tower stacks of Units 3 & 4.

Two standard high-volume air samplers (Misco Model 680), used to collect total suspended particulates (TSP), were run in sequence at each site. Each sampler employed an 8 x 10-inch quartz fiber filter (QATP, Pallflex Corporation) and was operated at a flow rate of about 1.3 m^3/min (45 cfm) for a sampling period of 48 hours. Samples were not collected if rain was forecasted.

Following sample collection, the loaded filters were folded in half, sealed in their original prelabeled ziplock bag, and stored in a freezer at The Geysers until transferred to PG&E at the end of the study. At PG&E, the samples were stored in a freezer for up to one month, until they were analyzed.

Previous studies of arsenic at The Geysers have measured concentrations of total arsenic in the soil, condensate and cooling tower waters and residues, and in atmospheric aerosols in or near the geothermal development area. Arsenic speciation results were obtained only for the steam condensate and cooling tower waters. A brief summary of these studies was prepared by PG&E (Gans and Solomon 1990).

The atmospheric measurements of arsenic at The Geysers were performed by PG&E as part of The Geysers Air Monitoring Program (GAMP) during 1983/1984 and 1986/1987. GAMP sampling sites were located in Glenbrook and Anderson Springs, two communities situated just outside of The Geysers geothermal development area.

Total (standard high-volume air sampler) and size-fractionated (dichotomous virtual impactor; fine <2.5 µm and coarse 2.5-10 µm aerodynamic diameter particles) 24-hour samples of atmospheric particulate matter were collected at each site every sixth day during two 1-year periods (1983/1984 and 1986/1987).

The high-volume air samples were stored for future analysis, whereas the fine and coarse particle samples were analyzed using x-ray fluorescence spectroscopy (XRF), a method capable of determining only total arsenic and not the individual species. The statistically defined detection limit for the XRF analysis was only about 3 ng m^{-3}, and most of the reported data were below this value. Of the 500 fine and coarse samples collected, only 12 (2.4%) were greater than the detection limit and all of those were observed in the fine particle samples: 11 at Anderson Springs and 1 at Glenbrook. The maximum and second highest values reported were 14 and 6 ng m^{-3}, respectively. Depending on how zero values are interpreted (e.g., equal to the detection limit, half the detection limit, or as reported), annual average concentrations of arsenic ranged from less than 1 ng m^{-3} to 3.3 ng m^{-3} at both sites. The ARB summarizes the GAMP data and reports monthly average values ranging from 1-4 ng m^{-3} and annual average values ranging from 1 to 2 ng m^{-3} (ARB 1990b). Applying these concentrations to the unit risk factors reported by the ARB, the estimated number of excess cancer deaths due to airborne inorganic arsenic exposure at The Geysers would be from <1 to 26 cases per ng m^{-3} per million persons. The lower end of the range (1-3) corresponds to nonsmokers, whereas the upper end (11-26) to males who smoke heavily. This risk is greater than one in a million, and therefore, airborne arsenic at The Geysers may concern the ARB.

The ambient average arsenic concentration data collected at The Geysers during GAMP, may be artificially high because of the poor analytical detection limit of the method used to analyze the fine and coarse filter samples. In addition, arsenic speciation data were not obtained during GAMP. This is important because As(III) is more toxic and may represent a greater carcinogenic hazard than As(V), and the ARB and EPA health risk assessments (ARB 1990c, EPA 1984) assume only As(III) is present in ambient aerosols. Therefore, the risk due to airborne inorganic arsenic at The Geysers is probably lower than determined from the GAMP data.

SAMPLE PREPARATION AND ANALYSIS

The analytical method developed by Solomon (1984) was used for determining the concentration of the inorganic species of arsenic (arsenite and arsenate) in atmospheric particulate matter. This sensitive method includes a semimicro sample preparation procedure for extracting the arsenic species from the filter, while maintaining the initial As(III)/As(V) ratio, and a species-specific analysis procedure for determining the concentrations of As(III) and As(V) in the sample extract.

Analysis Procedure

A complete description of the experimental conditions and protocol can be found in the literature (Solomon 1984). The procedure resulted in a routine (day-to-day) detection limit of about 15-25 ng for each species, similar to results reported previously (Solomon 1984, Rabano et al. 1989).

QUALITY ASSURANCE/QUALITY CONTROL

Quality assurance/quality control (QA/QC) procedures were implemented to ensure high quality data. Standard field and laboratory QA/QC procedures were followed and are summarized below.

Field Sampling

Multipoint calibrations of the flow rates for the high-volume air samplers were obtained before and after the study. This helped to ensure that filter clogging or other problems did not occur during the extended sampling period of 48 hours. After collection, samples were stored in their original prelabled ziplock bags at reduced temperatures (below 0°C) until analyzed. At all times, filters were handled with tweezers or talc-free gloves.

Chemical Analysis

The concentrations of all chemical species were determined by comparison to laboratory standards of known concentrations. Aqueous standards were diluted daily from more concentrated solutions prepared bimonthly from ACS-grade analytical reagents. The matrix of the daily standard matched that of the extraction solution.

Teflon vials containing 4.0 ml of 4.25 N HCl and known amounts of arsenite and arsenate (100 ng or 400 ng of each) were extracted and analyzed daily, along with the filter samples, to confirm that the arsenic species were stable and fully recovered throughout the sample extraction and analysis procedure.

For all samples, two identical portions from each filter were extracted in separate Teflon vials and analyzed separately as duplicates to obtain an estimate of the precision for the overall sample preparation and analysis procedure. Replicate analysis of the extract in each sample vial also was performed to ensure accurate and consistent results. Replicate values were first averaged and then duplicate values were averaged to determine the mean loading for an individual filter.

RESULTS AND DISCUSSION

Analytical Methods Evaluation

The sample preparation and analysis method for the determination of the inorganic species of arsenic (arsenite and arsenate) in atmospheric particulate matter (Solomon 1984) was evaluated by the Air Quality Unit at PG&E. The evaluation indicated that the method is capable of determining nanogram levels of As(III) and As(V), while maintaining the initial As(III)/As(V) ratio. The results are summarized in Gans and Solomon (1990).

Effect of Atmospheric Particles

A limited number of samples were analyzed to determine what effect the sample matrix might have on the recovery and stability of the As(III)/ As(V) ratio when atmospheric particles are present on the filter during analysis by the speciation method. The recovery of the standard additions was 60 ± 18% for As(III) and 102 ± 29% for As(V). These results are slightly different from those reported previously (Solomon 1984, Rabano et al. 1989). In the earlier studies, it was apparent that the presence of atmospheric particles on the filter caused 10-20% of the known addition of As(III) to be oxidized to As(V). In this study, it appears that 40% of the As(III), on the average, was lost during the sample preparation and analysis procedure, whereas As(V) was completely recovered. The As(III) values presented in this report were not corrected for this possible matrix effect.

The difference between this study and the previous work may be due to the low As(III) levels encountered at The Geysers or differences in the sample matrix (i.e., particle composition) at the different sampling locations. Further studies will be required to determine the cause of these observed small differences.

ATMOSPHERIC MEASUREMENTS

Atmospheric particulate matter samples were collected at The Geysers during 1989 and analyzed for As(III) and As(V) by the arsenic speciation method. (Solomon 1984).

1989 Total Suspended Particulate Matter (TSP) Samples

Table 1 presents the As(III) and As(V) concentrations (ng/m^3) measured in the TSP samples collected at the East and West Geysers sites during April and May 1989. In this table, the less-than values are equal to the atmospheric detection limit (ADL) calculated for that filter. Based on nominal conditions, the ADL is about 0.23 ng/m^3. It varies because the analytical detection limit, flow rates, and sampling time varied slightly from sample to sample.

The errors listed in Table 1 for values greater than the LOD were determined by propagating the average precision for the analysis and for the sample volume. The overall average analysis precision, defined as the average coefficient of variation and based on the duplicate and replicate analyses, was 12% for As(III) and 13% for As(V). These values reflect the precision near the detection limit of the method, because most of the measurable values are near the LOD of the analysis procedure. The average sample volume precision was estimated to be 3%. For values that were measurable, but less than the detection limit, the stated error is equal to the detection limit for that sample.

In general, As(III) and As(V) levels were higher at the East Geysers site than at the West Geysers. Average concentrations at the East Geysers for As(III) and As(V) were 0.54 ng/m^3 and 2.9 ng/m^3, respectively. At the East Geysers, only two samples had As(III) concentrations greater than 1 ng/m^3, while most As(V) values were greater than 1 ng/m^3. At the West Geysers, average concentrations were generally less than the detection limit for As(III) and about equal to 0.46 ng/m^3 for As(V). Only one sample at the West Geysers was above 1 ng/m^3. The highest (As(III) = 3.08 ng/m^3; As(V) = 6.54 ng/m^3) and second highest (As(III) = 1.51 ng/m^3; As(V) = 5.96 ng/m^3) values for both species were observed at the East Geysers on April 15-16 and on May 18-19, respectively. No unusual conditions were reported for either date.

Time series plots of the As(III) and As(V) concentrations observed at the two monitoring sites indicate differences in arsenic concentrations at both sites.

At the East Geysers, As(III) and As(V) track each other closely (0.83). This observation suggests either similar sources for both species, or more likely, similar variations in meteorologic conditions that are controlling the atmospheric loadings of arsenic in the air. It is not known if a similar situation exists at the West Geysers, since the As(III) concentrations were below the detection limit.

The differences in arsenic concentrations observed between the two sites may be due to local meteorology (e.g., the East Geysers site may have been below the inversion layer more often because it was 50 ft above the valley floor, whereas the West Geysers site was 600 ft above the valley floor) or the impact of the different sources in the area. Other reasons also may exist; however, the reasons for the differences cannot be determined from this limited data set.

Total arsenic, equal to the sum of As(III) and As(V), ranged from less than the detection limit to 9.6 ng/m^3, with an average value of 2.6 ng/m^3 at the East Geysers and 0.69 ng/m^3 at the West Geysers. These averages include less-than values as equal to the stated detection limit for that sample. Total arsenic concentrations observed in April and May during the 1983/1984 and 1986/1987 GAMP program ranged from less than the detection limit to 6 ng/m^3. It is difficult to define an average for these samples, because most of the samples were less than the detection limit of 3 ng/m^3.

Atmospheric levels of arsenic observed during this study appear to be similar to those observed during GAMP (i.e., most samples were less than 3 ng/m^3, with only a few values greater than 3 ng/m^3). However, it should be remembered that the 1989 samples were collected within The Geysers geothermal development area, whereas the GAMP samples were collected near two communities outside The Geysers. In addition, the 1989 samples were collected to maximize filter loadings by not sampling when rain was forecasted and by locating the samplers at sites expected to be below the inversion layer, if one developed. Therefore, the 1989 data likely

represents a maximum for arsenic concentrations in the area during the study period. Additional sampling at sites within and external to The Geysers geothermal development area could define what differences exist between the various locations.

The averages reported here are consistent with averages reported by the ARB (ARB 1990b, 1990c) for the State of California. The ARB reports a statewide average of about 1.5 ng/m^3, and northern and southern California averages of 1.2 and 2.0 ng/m^3, respectively.

The ratio of As(III)/As(V) is presented in Table 1. The average ratio for the East Geysers was 0.21 with a maximum value of 0.47. An average value for the West Geysers could not be calculated, because most of the As(III) values were below the detection limit of 0.2 ng m^{-3}. These results are similar to those observed previously (Solomon 1984, Rabano et al. 1989) and indicate that both As(III) and As(V) are present in the atmospheric aerosol. More important, these results indicate that most arsenic at The Geysers is in the +5 (i.e., As(V)) oxidation state or in the potentially less toxic form.

Table 1. As(III) and As(V) Concentrations at East and West Geysers sampling sites.[a]

Site	Date	As(III) ng/m^3	As(V) ng/m^3	As(III)/As(V)
East Geysers	890411	0.17 ± 0.23	1.68 ± 0.22	0.10
	890413	0.47 ± 0.06	4.26 ± 0.56	0.11
	890415	3.08 ± 0.40	6.54 ± 0.86	0.47
	890417	0.23 ± 0.31	3.94 ± 0.52	0.06
	890419	0.46 ± 0.06	2.31 ± 0.30	0.20
	890421	0.17 ± 0.17	0.84 ± 0.11	0.20
	890423	0.17 ± 0.21	0.70 ± 0.09	0.24
	890429	0.06 ± 0.21	0.51 ± 0.07	0.12
	890501	0.46 ± 0.06	1.22 ± 0.16	0.38
	890503	0.14 ± 0.21	1.14 ± 0.15	0.12
	890505	0.18 ± 0.31	0.96 ± 0.13	0.19
	890508	0.52 ± 0.07	2.20 ± 0.29	0.24
	890511	0.29 ± 0.32	1.13 ± 0.15	0.26
	890513	0.22 ± 0.22	1.24 ± 0.16	0.18
	890515	0.08 ± 0.32	1.39 ± 0.18	0.06
	890518	1.51 ± 0.20	5.96 ± 0.79	0.25
	890520	0.98 ± 0.13	2.99 ± 0.39	0.33
	$x \pm \sigma$	0.54 ± 0.75	2.29 ± 1.84	0.21 ± 0.11
West Geysers	890405	< 0.18	0.30 ± 0.04	-
	890407	< 0.25	0.35 ± 0.04	-
	890410	0.08 ± 0.18	0.74 ± 0.09	0.11
	890412	< 0.22	1.30 ± 0.17	-
	890414	0.09 ± 0.19	0.95 ± 0.12	0.09
	890416	0.19 ± 0.22	0.68 ± 0.09	0.28
	890418	< 0.24	0.17 ± 0.24	-
	890420	< 0.28	0.18 ± 0.28	-
	890422	< 0.24	0.26 ± 0.03	-
	890426	< 0.23	0.41 ± 0.05	-
	890428	< 0.30	0.59 ± 0.08	-
	890502	< 0.25	0.35 ± 0.04	-
	890504	< 0.30	0.08 ± 0.30	-
	890507	< 0.28	0.84 ± 0.11	-
	890509	< 0.24	0.27 ± 0.03	-
	890511	< 0.07 ± 0.24	0.21 ± 0.24	0.33
	890513	< 0.26	0.29 ± 0.04	-
	890517	< 0.25	0.28 ± 0.04	-
	890519	< 0.27	0.46 ± 0.06	-
	$x \pm \sigma$[b]	0.22 ± 0.07	0.46 ± 0.32	0.20 ± 0.12
	$x \pm \sigma$[c]	0.02 ± 0.05	———	———

[a]For less-than values (<), the error represents the detection limit for that sample. For samples where the error is greater than the sample value, the sample value was detected, but less than the detection limit (defined as twice the baseline noise), which is given as the error for that sample. Other errors are calculated based on the propagation of the analysis and sampling precisions.

[b]Upper limit, includes less-than values (<) as equal to the value given (i.e., the detection limit for that sample); all other values are included as given. For the AS(III)/As(V) ratio, the average includes only the value given.

[c]Lower limit, includes less-than values (<) as equal to zero; all other values are included as given.

CONCLUSIONS

The enactment of new regulations regarding air toxics along with ARB's report entitled "Public Exposure to Airborne Inorganic Arsenic in California" suggests that geothermal energy producers in California must remain aware of the current atmospheric levels of arsenic at The Geysers. These producers must also be able to provide evidence of the species-specific nature of the airborne arsenic if the regulatory climate changes to include the inorganic species of arsenic in health risk assessment calculations.

A method for the determining the inorganic species of arsenic (arsenite, As(III) and arsenate, As(V)) was evaluated and found to be capable of determining sub-nanogram levels of As(III) and As(V) in atmospheric particulate matter, while maintaining the initial As(III)/As(V) ratio in the aerosol collected on the filter. An atmospheric detection limit of approximately 0.2 ng/m^3 was obtained for both species.

It was determined that the aerosol matrix (i.e., composition of the collected particles) appears to interfere with the procedure by reducing the As(III) response by an average of about 40%. This effect can be compensated for by applying the method of standard additions. The As(V) response appears unaffected.

Arsenic(III) concentrations ranged from less than the detection limit (0.2 ng m^{-3} to about 3 ng/m^3, with an overall average for both sites of about 0.26-0.46 ng/m^3 depending on how values less than the detection are included in the calculation. The lower limit assumes less-than values as equal to zero and the upper limit assumes less-than values as equal to the detection limit. Arsenic(V) concentrations ranged from less than the detection limit (0.2 ng m^{-3}), but measurable, to about 6.5 ng/m^3, with an overall average for both sites of about 1.3 ng/m^3. Concentrations of both species were higher at the East Geysers site than at the West Geysers site.

Total arsenic concentrations ranged from the detection limit (0.2 ng m^{-3}) to about 9.6 ng/m^3, with an average for both sites equal to about 1.6 ng/m^3. This average value is very close to the statewide average of 1.5 ng/m^3, as determined by the ARB (ARB 1990b). These data would therefore suggest that The Geysers may not be an area of significant concern with regard to atmospheric arsenic concentrations, relative to the rest of California.

The average As(III)/As(V) ratio at the East Geysers was 0.21. The ratio was variable and ranged up to 0.47. An average ratio for the West Geysers site could not be determined, because most As(III) values at that site were below the detection limit of the method. These data indicate that As(V) was the dominant arsenic species and on the average equal to greater than 83% of the total arsenic measured. This may be important if future health risk assessments are based on the individual species of arsenic and not on total arsenic, as was recently done by the California Department of Health Services (ARB 1990c). One result of such a change may be to allow exemptions or amendments to some of the operations at The Geysers, which could reduce the financial impact of compliance on energy producers using geothermal power plants. It is suggested that this preliminary study be considered as a baseline to provide an indication of concentration levels. These results also can be used to support recommendations for a long-term study of arsenic at The Geysers, if the regulatory climate changes from requiring total to species-specific data on arsenic in the atmosphere.

ACKNOWLEDGMENTS

We wish to thank Carol Coppedge and Bill Hunt for operating the field sites during the study and Ron Suess and Dan Felperin for arranging for aerosol samples to be collected within The Geysers geothermal development area. We also wish to thank Ted Arcado for providing quality assurance/quality control for the field portion of the study. Much appreciation also is extended to Rich McCurdy and Gary Sharp, who allowed us to establish the arsenic speciation procedure in their chemistry laboratory at PG&E.

REFERENCES

Anderson, D., 1986. Review and evaluation of arsenic at The Geysers, Phase A: Summary of current information. Prepared by Steam Generation Department. Prepared for Research, Development, and Demonstration. Pacific Gas and Electric Company, San Ramon, CA.

Andreae, M. O., 1980. Arsenic in rain and the atmospheric mass balance of arsenic. J. Geophys. Res. 85:4512.

Appel, B. R., Y. Tokiwa, and E. M. Hoffer, 1984. Efficiency of filter sampling for arsenic in the atmosphere. Atmos. Environ. 18:219.

California Air Resources Board, 1990a. Status of Toxic Air Contaminant Identification. California Air Resources Board, Sacramento, CA.

California Air Resources Board, 1990b. Public exposure to airborne inorganic arsenic in California, final report to the Air Resources Board on Inorganic Arsenic, Part A. California Air Resources Board, Sacramento, CA.

California Air Resources Board. 1990c. Health Effects of Arsenic Compounds, final report to the Air Resources Board on Inorganic Arsenic, Part B. California Air Resources Board, Sacramento, CA.

California Department of Health Services. 1984. Health and Safety Code, Sections 39650 et seq., Food and Agriculture Code Sections 14021 et seq. California State Law Library, Sacramento, CA.

California Department of Health Services. 1987. Health and Safety Code, Sections 44321 et seq., California State Law Library, Sacramento, CA.

Environmental Protection Agency. 1971. National primary and secondary ambient air quality standards. Environmental Protection Agency. Federal Register, 36:8186.

Environmental Protection Agency. 1978. An Assessment of the Health Effects of Arsenic Germane to Low-Level Exposure. Environmental Protection Agency, Office of Research and Development. Washington, D.C.

Environmental Protection Agency. 1984. Health Assessment Document for Inorganic Arsenic, Report No. EPA-600/8-83-021F.

Gans, C. D. and P.A. Solomon. 1990. Arsenic Speciation in Atmospheric Aerosols at The Geysers. Environment, Health & Safety, No. 009.1-89.3, Department of Research and Development, Pacific Gas and Electric Company, San Ramon, CA.

Geysers Air Monitoring Program. 1982. Memorandum of understanding for The Geysers Air Monitoring Program. Northern Sonoma County Air Quality Management District.

Hemberg, S. 1972. Origins of human cancer. Vol. 4. Ed. by H. H. Hiatt. Cold Spring Harbor Laboratories, New York, p. 147.

Johnson, D. L. and R. S. Braman. 1975. Alkyl- and inorganic arsenic in air samples. Chemosphere 6:333.

Lisk, D. J. 1971. Ecological aspects of metals. N.Y. St. J. Med. 71:2541.

Maenhaut, W., W. H. Zoller, R. A. Duce, and G. L. Hoffman. 1979. Concentration and size distribution of particulate trace elements in the south polar atmosphere. J. Geophys. Res. 84:2421.

Nakamura, M., Y. Matsuzono, S. Tanaka, and Y. Hashimoto. 1989. Chemical form of arsenic compounds and distribution of their concentrations in marine atmospheres. The Chemical Society of Japan. 2:227.

National Academy of Science. 1971. Medical and Biological Effects of Environmental Pollutants: Arsenic. National Academy of Science, Washington, D.C. p. 117, 195.

Rabano, E. S., N. T. Castillo, K. J. Torre, and P. A. Solomon. 1989. Speciation of arsenic in ambient aerosols collected in Los Angeles, J. Air Pollution Control Assoc. 39:76.

Sawicki, E. 1967. Airborne carcinogens and allied compounds. Arch. Environ. Health. 14:46.

Solomon, P. A. 1984. Collection and Analysis Techniques for Studies of Atmospheric Arsenic Species. Ph.D. thesis, Department of Chemistry, University of Arizona, Tucson, Arizona.

Walsh, P. R., R. A. Duce, and J. L. Fasching. 1977. Impregnated filter sampling system for collection of volatile arsenic in the atmosphere. Environ. Sci. and Technol. 11:163.

Walsh, P. R., R. A. Duce, and J. L. Fasching. 1979. Tropospheric arsenic over marine and continental regions. J. Geophys, Res. 84:1710.